

Synthesis and Decomposition of a Novel Carboxylate Precursor to Indium Oxide

Aloysius F. Hepp and Maria T. Andras
Lewis Research Center
Cleveland, Ohio

Stan A. Duraj
Cleveland State University
Cleveland, Ohio

Eric B. Clark
Lewis Research Center
Cleveland, Ohio

David G. Hehemann
Kent State University
Kent, Ohio

Daniel A. Scheiman
Sverdrup Technology, Inc.
Brook Park, Ohio

Phillip E. Fanwick
Purdue University
West Lafayette, Indiana

Prepared for the
Fall Meeting
sponsored by the Materials Research Society
Boston, Massachusetts, November 29–December 3, 1993



National Aeronautics and
Space Administration

N95-12693

Unclass

G3/23 0017062

(NASA-TM-106555) SYNTHESIS AND
DECOMPOSITION OF A NOVEL
CARBOXYLATE PRECURSOR TO INDIUM
OXIDE (NASA. Lewis Research
Center) 8 p

SYNTHESIS AND DECOMPOSITION OF A NOVEL CARBOXYLATE PRECURSOR TO INDIUM OXIDE

ALOYSIUS F. HEPP,* MARIA T. ANDRAS,*† STAN A. DURAJ,** ERIC B. CLARK,* DAVID G. HEHEMANN,***,†† DANIEL A. SCHEIMAN,† AND PHILLIP E. FANWICK††

*NASA Lewis Research Center, Photovoltaic Branch, M.S. 302-1, Cleveland, OH 44135

**Department of Chemistry, Cleveland State University, Cleveland, OH, 44115

***School of Technology, Kent State University, Kent, OH 44242

†Sverdrup Technology, Inc., 2001 Aerospace Parkway, Brook Park, OH 44142

††Department of Chemistry, Purdue University, West Lafayette, IN 47907

ABSTRACT

Reaction of metallic indium with benzoyl peroxide in 4-methylpyridine (4-Mepy) at 25 °C produces an eight-coordinate mononuclear indium(III) benzoate, $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2 \cdot 4\text{H}_2\text{O}$ (I), in yields of up to 60%. The indium(III) benzoate was fully characterized by elemental analysis, spectroscopy, and X-ray crystallography; (I) exists in the crystalline state as discrete eight-coordinate molecules; the coordination sphere around the central indium atom is best described as pseudo-square pyramidal. Thermogravimetric analysis of (I) and X-ray diffraction powder studies on the resulting pyrolysate demonstrate that this new benzoate is an inorganic precursor to indium oxide. Decomposition of (I) occurs first by loss of 4-methylpyridine ligands (100°-200°C), then loss of benzoates with formation of In_2O_3 at 450°C. We discuss both use of carboxylates as precursors and our approach to their preparation.

INTRODUCTION

Our interest in oxygen-containing gallium and indium complexes derives from efforts to produce precursors for deposition of thin-film materials for solar cell fabrication [1]. Oxides are deposited or grown on solar cells to provide electrical insulation, to decrease surface recombination, or to produce anti-reflective coatings [2]. A major issue surrounding technological applications of InP is the deposition of insulators on the surface that are chemically stable with good electrical and interfacial properties. With this goal in mind, we are searching for easy to prepare and handle chemical vapor deposition (CVD) precursors to In_2O_3 . Recently, we reported the preparation and characterization of the first main group oxo-centered trimeric carboxylate, $[\text{Ga}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CC}_6\text{H}_5)_6(4\text{-Mepy})_3][\text{GaCl}_4]$ [3]. In an attempt to prepare a monomeric indium benzoate, we reacted indium metal with benzoyl peroxide in 4-methylpyridine at 25 °C and obtained $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$ (4-Mepy = 4-methylpyridine) (I) in good yields.

The existence of indium and gallium carboxylates is well-documented [4,5]. Numerous homoleptic polynuclear indium(III) carboxylates, $[\text{In}(\text{O}_2\text{CR})_3]_x$ (R = H, CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, $(\text{CH}_3)_2\text{CH}$, and $(\text{CH}_3)_3\text{C}$) [6], as well as polynuclear organoindium(III) carboxylates, $[\text{R}_2\text{In}(\text{O}_2\text{CR}')_3]_x$ (R = CH_3 , C_2H_5 , $\text{R}' = \text{CH}_3$, C_2H_5 or R = $n\text{-C}_4\text{H}_9$, $\text{R}' = \text{C}_2\text{H}_5$) are known [6-10]; however, there is a void in the literature on analogous indium(III) benzoates. To the best of our knowledge, $\text{Cl}_2\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)\text{py}_2$ (py = pyridine), a six-coordinate mononuclear species, is the only structurally characterized indium(III) benzoato complex to date [11]. We describe the synthesis, structure and mass spectral analysis of the eight-coordinate mononuclear indium(III) benzoato complex (I). Thermogravimetric analysis (TGA) of (I) and X-ray diffraction powder (XRD) studies on the resulting pyrolysate demonstrate that this new benzoate is a precursor to indium (III) oxide, In_2O_3 .

‡ - National Research Council/NASA Lewis Research Center Resident Research Associate.

†† - Senior Research Fellow/NASA Lewis Research Center Resident Research Associate.

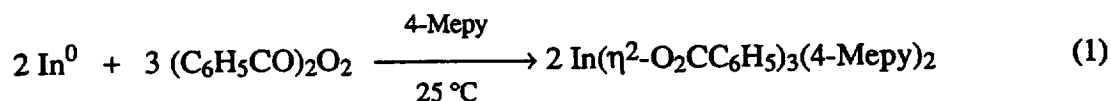
EXPERIMENTAL

All operations of moisture- and air-sensitive materials were performed under an inert atmosphere using standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. drybox equipped with a HE-493 dri-train. Solvents were freshly distilled from sodium benzophenone ketyl prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Indium powder (Aldrich) was used without additional purification. Benzoyl peroxide was deaerated under vacuum at room temperature. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Inc. (Knoxville, TN). Thermogravimetric analyses were performed under an atmosphere of nitrogen using a Perkin Elmer TGS-II. Powder X-ray diffraction (XRD) data was collected using monochromated Cu K α radiation on a Scintag PAD V and a Phillips APD diffractometer. Electron impact mass spectra were recorded on a Finnigan TSQ-45 mass spectrometer. X-ray diffraction data were collected at 20 \pm 1 $^{\circ}$ C on a 0.38 x 0.38 x 0.31 mm crystal using an Enraf-Nonius CAD-4 diffractometer.

In(η^2 -O₂CC₆H₅)₃(4-Mepy)₂ was prepared by reaction of 150-mesh indium powder (0.50 g, 4.35 mmol) and benzoyl peroxide (1.58 g, 6.52 mmol) in 35 mL of 4-methylpyridine at ambient temperature for several days. The mixture was filtered, and the resulting off-white solid washed with three 25 mL aliquots of hexane and dried under vacuum for 2 h. Hexane, 150 mL, was added to the bright yellow filtrate to further precipitate the white solid. The supernatant was decanted, and the white solid was washed with two 25 mL aliquots of fresh hexane and dried under vacuum for 2 h. The solids were combined, recrystallized from 4-methylpyridine/hexane (v/v 40/70) and dried under vacuum for 18 h, the yield is 53-60%. The analytical data was consistent with the single crystal X-ray structure and is detailed in a prior publication [12].

RESULTS AND DISCUSSION

Oxidation of indium metal by benzoyl peroxide in 4-methylpyridine produces the first mononuclear indium(III) benzoate in yields of up to 60% (Eq. 1):



In(η^2 -O₂CC₆H₅)₃(4-Mepy)₂ is very stable; it can be stored under an inert atmosphere at room temperature for extended periods of time. TGA studies show that it is thermally stable up to 100 $^{\circ}$ C, at this temperature loss of 4-methylpyridine occurs. In contrast, pyridine adducts of indium(III) acetate and formate are unstable, losing pyridine slowly at room temperature [13].

Colorless single crystals, suitable for X-ray diffraction studies, were grown by slow interdiffusion of hexane into a 4-methylpyridine solution of (I), the compound crystallized as the tetrahydrate (I)·4H₂O, no doubt from trace amounts of water in the coordinating solvent. Crystallographic data are summarized in Table 1, a detailed description of the structural analysis is given in [12]. Single crystal X-ray diffraction analysis reveals that (I)·4H₂O is composed of an ordered array of discrete mononuclear eight-coordinate molecules positioned on a crystallographic two-fold rotation axis. The solid-state molecular structure of (I) is shown in Figure 1. The immediate coordination sphere around the central indium(III) atom is best described as a pseudo-square pyramid with each bidentate benzoate assuming a single position. The In atom is bound to six oxygen atoms from three equivalent (vide infra) bidentate benzoate groups. The In-O bond distances range from 2.225(6) to 2.413(5) Å. Within the symmetrically independent benzoate ligand, the In-O bond lengths are not equivalent. The In-O(22) bond length, 2.413(5) Å, is slightly longer (by 0.19 Å) than the In-O(21) bond length, 2.225(6) Å. Unsymmetrical bonding of chelating carboxylate groups to an indium(III) center is not unusual [14].

TABLE 1.
Crystallographic Data for $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2 \cdot 4\text{H}_2\text{O}$.

chemical formula $\text{InO}_{10}\text{N}_2\text{C}_{33}\text{H}_{37}$	formula weight 736.49
$a = 11.7195(8) \text{ \AA}$	space group C2/c (No. 15)
$b = 11.995(1) \text{ \AA}$	$T = 20^\circ\text{C}$
$c = 25.407(2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$\beta = 94.177(6)^\circ$	$\rho_{\text{calc}} = 1.373 \text{ g cm}^{-3}$
$V = 3562.0(8) \text{ \AA}^3$	$\mu(\text{Mo K}\alpha) = 7.04 \text{ cm}^{-1}$
$Z = 4$	$R(F_o)^a = 0.059$
	$R_w(F_o)^b = 0.079$

^a $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $R_w(F_o) = [\sum w|F_o| - |F_c|]^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

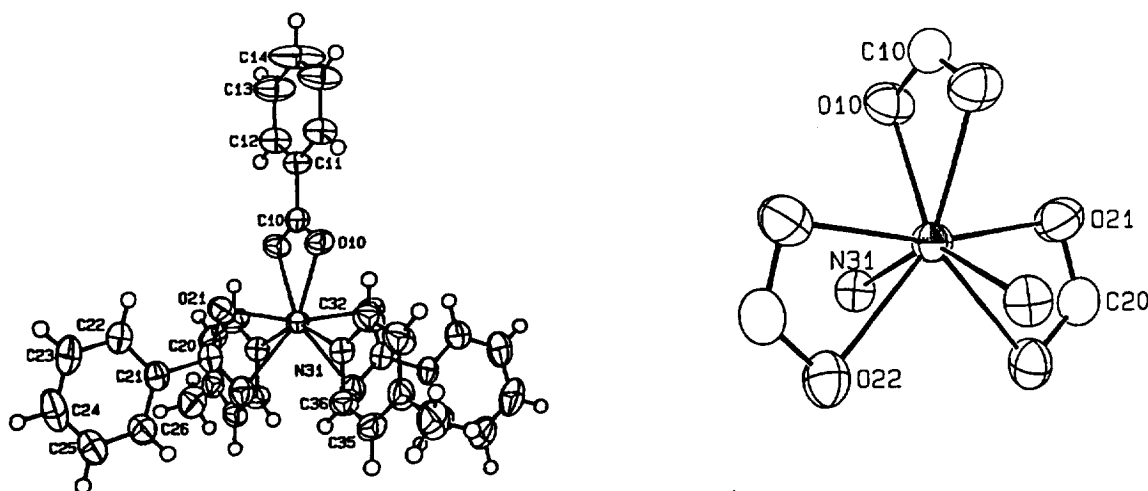


Figure 1. ORTEP drawing of the $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$ molecule showing 50% thermal ellipsoids and the atomic labeling scheme. Compound (I) InO_6N_2 core on right.

A common reactivity/bonding characteristic of indium(III) complexes is the expansion of the indium(III) atom coordination sphere through polymerization or adduct formation [6-15]. In the case of indium(III) carboxylates (of which (I) is an example), the coordination number of the indium(III) atom generally increases to 6 or 8 via polymerization of the $[\text{In}(\text{OOCR})_3]$ units - oxygen atoms from adjacent carboxylate molecules bridge the units creating infinite $[\text{In}(\text{OOCR})_3]_n$ chains. In (I), the presence of the two methylpyridine ligands prevents such polymerization by coordinatively saturating the indium(III) atom, resulting in the formation of the first mononuclear eight-coordinate indium(III) benzoato species. The tendency to associate can be seen by the complete lack of parent ions in mass spectra with 25 and 70 eV ionization. The most intense peaks in the spectra, with m/e values: 105 and 77, correspond to loss of O and CO_2 from the benzoate group to form C_6H_5^+ and $\text{C}_6\text{H}_5(\text{CO})^+$ ions. While much less intense, the strongest metal-containing ion peaks, in decending intensity order are m/e (for ^{115}In): 357, 313, 115, 269, 435, 479, these peaks can be assigned to, respectively: $\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_2^+$, $\text{C}_6\text{H}_5\text{In}(\text{O}_2\text{CC}_6\text{H}_5)^+$, In^+ , $(\text{C}_6\text{H}_5)_2\text{In}^+$, $(\text{C}_6\text{H}_5)\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_2^+$, and $\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_3^+$. While the volatility of (I) is low at decomposition, the compound readily produces In_2O_3 .

Thermal decomposition of $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$ was followed by TGA in both air and nitrogen, and the composition of the final pyrolysate determined by XRD. No attempt was made to identify the intermediate pyrolysates produced during this analysis. The first two steps in the thermogram (see Figure 2) correspond to the sequential loss of the two 4-methylpyridine ligands. The same results were obtained in air and nitrogen. This lack of effect on the formation of oxide is expected due to the InO_6N_2 coordination environment around indium, it is also consistent with the ready decomposition of benzoate seen in the mass spectra.

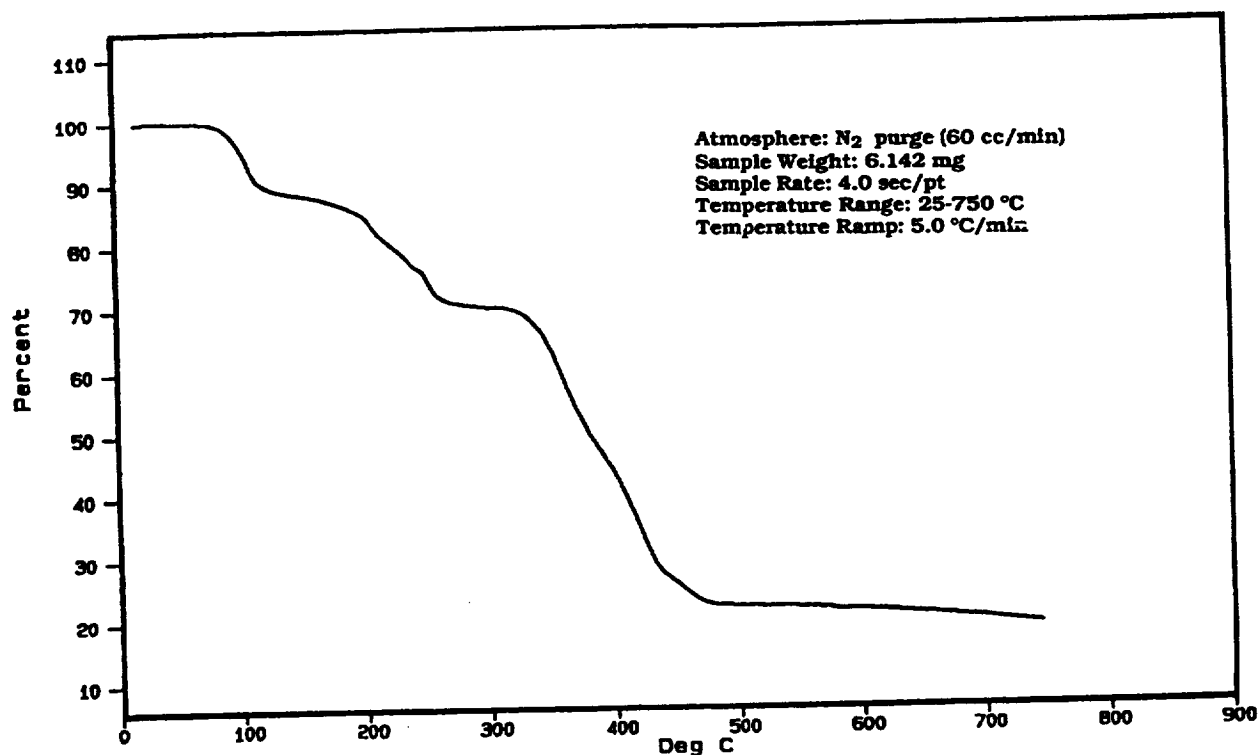


Figure 2. Thermogravimetric analysis of $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$ under an atmosphere of nitrogen. The theoretical values for weight changes are: 86%, $[\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2 - (4\text{-Mepy})]$; 72%, $[\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2 - 2(4\text{-Mepy})]$; 21%, $\text{In}_2\text{O}_3/\text{In}(\text{O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$.

The final weight loss corresponds to complete decomposition of $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$ to In_2O_3 , as demonstrated by weight loss and XRD pattern, Table 2 [16,17]. The most interesting aspect of the TGA data is the relatively low temperature (475 °C) for the stabilization of weight loss. By contrast, the polymeric $\text{In}(\eta^2\text{-O}_2\text{CCH}_3)_n$ [13], did not reach a stable mass until between 1000 and 1100 °C, above the sublimation temperature of In_2O_3 of 850 °C [18]. No attempt was made to characterize the intermediate materials. The morphology of material produced during a typical thermal analysis run is shown in a scanning electron micrograph, figure 3. As can be seen, melting has occurred in the material, as the temperature of the sample reached 750 °C; this is still 300 °C below the temperature needed to fully convert the polymeric acetate [13].

TABLE 2.

X-ray Diffraction (XRD) Powder Pattern for Pyrolysate, In_2O_3 ,
Between 1.20 and 5.00 Å.

Angle, 2θ	d, Å	I/I _{max} , %
21.522	4.126	1.18
30.750	2.905	100.00
35.510	2.53	35.19
37.725	2.383	3.48
41.895	2.155	11.72
45.710	1.983	6.64
49.302	1.847	3.11
51.115	1.786	65.64
52.745	1.734	2.99
56.075	1.638	7.54
59.200	1.56	8.30
60.675	1.525	58.17
52.222	1.491	13.16
63.700	1.46	12.67
65.198	1.43	4.85
68.030	1.377	8.11
69.475	1.351	5.16
73.745	1.284	5.63
75.102	1.264	8.50
76.272	1.247	7.92

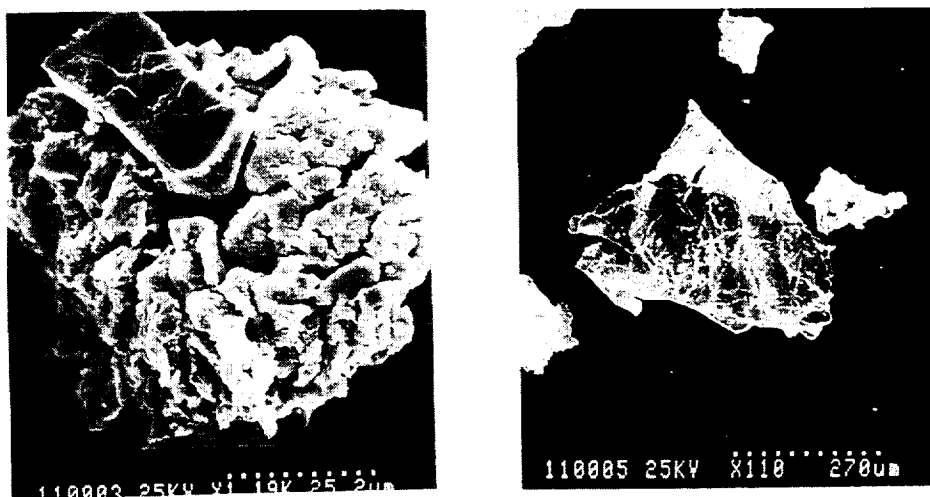


Figure 3. Scanning electron micrographs of typical samples of In_2O_3 produced during TGA experiments and characterized by XRD, see text.

CONCLUSIONS

We have demonstrated a simple and direct one-step route to $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2$, the first mononuclear eight-coordinate indium(III) benzoate. Our approach to the synthesis of indium(III) carboxylates differs significantly from previously reported methods [4-11]. The presence of 4-methylpyridine at the initial stages of reaction virtually eliminates all probability of $\text{In}(\text{O}_2\text{CR})_3$ polymerization by coordinatively saturating the indium(III) center as it is formed. In addition, we have established that (I) is a stable inorganic precursor to indium oxide.

ACKNOWLEDGEMENT

A.F.H. (Director's Discretionary Fund), M.T.A. (Postdoctoral Fellowship, National Research Council/NASA Lewis Research Center), S.A.D. (NASA Cooperative Agreement NCC3-162), D.G.H. (NASA Cooperative Agreement NCC3-318), and P.E.F (NASA Cooperative Agreement NCC3-246) acknowledge support from NASA Lewis Research Center. We thank Ms. Ruth Cipicic (XRD, NASA LeRC) and Mr. Frederick K. Oplinger (NMR, CSU) for assistance.

REFERENCES

1. I. Weinberg, *Solar Cells* **29**, 225 (1990).
2. J. van de Ven, J.J.M. Binsma, and N.M.A. de Wild, *J. Appl. Phys.* **67**, 7568 (1990).
3. M.T. Andras, S.A. Duraj, A.F. Hepp, P.E. Fanwick, and M.M. Bodnar, *J. Am. Chem. Soc.* **114**, 786 (1992).
4. R.C. Mehrotra and R. Bohra, *Metal Carboxylates*; (Academic Press, London, 1983) pp. 121-129, 178-181.
5. D.G. Tuck, in *Comprehensive Organometallic Chemistry; Vol. 1*, edited by G. Wilkinson, F.G.A. Stone, E.W. Abel, (Pergamon Press, New York, 1982) pg. 719.
6. V.W. Lindel and F.Z. Huber, *Anorg. Allg. Chem.* **408**, 167 (1974).
7. H.D. Hausen, *J. Organometal. Chem.* **39**, C37 (1972).
8. F.W.B. Einstein, M.M. Gilbert, and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 248 (1973).
9. J.J. Habeeb and D.G. Tuck, *Can. J. Chem.* **52**, 3950 (1974).
10. R. Nomura, S. Fujii, K. Kanaya, and H. Matsuda, *Polyhedron* **9**, 361 (1990).
11. M.A. Khan, C. Peppe, and D.G. Tuck, *Acta Cryst.* **C39**, 1339 (1983).
12. M.T. Andras, A.F. Hepp, S.A. Duraj, E.B. Clark, D.A. Scheiman, D.G. Hehemann, and P.E. Fanwick, *Inorg. Chem.* **32**, 4150 (1993).
13. J.J. Habeeb and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 243 (1973).
14. For example, $\text{In}(\text{O}_2\text{CMe})_3\text{L}$ where L is a bidentate N, N'-donor molecule, i.e., 2,2' bipyridine or 1,10-phenanthroline; see V.H. Preut and F.Z. Huber, *Anorg. Allg. Chem.* **450**, 120 (1979).
15. R. Kumar, H.E. Mabrouk, and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1045 (1988).
16. The diffraction pattern was matched with In_2O_3 in the JCPDS International Center for Diffraction Data 1989. Powder Diffraction File No. 6-0416.
17. Chemical analysis showed total C, H, and N content below detection limit.
18. *Handbook of Chemistry and Physics*, edited by R.C. Weast, 55th ed. (Chemical Rubber Company Press, Cleveland, OH, 1974) pg. B-96.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE July 1994		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE Synthesis and Decomposition of a Novel Carboxylate Precursor to Indium Oxide			5. FUNDING NUMBERS WU-233-01-0A	
6. AUTHOR(S) Aloysius F. Hepp, Maria T. Andras, Stan A. Duraj, Eric B. Clark, David G. Hehemann, Daniel A. Scheiman, and Phillip E. Fanwick				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-8715	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, D.C. 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-106555	
11. SUPPLEMENTARY NOTES Prepared for the Fall Meeting sponsored by the Materials Research Society, Boston, Massachusetts, November 29-December 3, 1993. Aloysius F. Hepp and Eric B. Clark, NASA Lewis Research Center; Maria T. Andras, National Research Council—NASA Research Associate at Lewis Research Center; Stan A. Duraj, Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115 (work funded by NASA Cooperative Agreement NCC3-162); David G. Hehemann, School of Technology, Kent State University, Kent, Ohio 44242, and Senior Research Fellow—NASA Resident Research Associate at Lewis Research Center (work funded by NASA Cooperative Agreement NCC3-318); Daniel A. Scheiman, Sverdrup Technology, Inc., Lewis Research Center Group, 2001 Aerospace Parkway, Brook Park, Ohio 44142 (work funded by NASA Contract NAS3-25266); and Phillip E. Fanwick, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (work funded by NASA Cooperative Agreement NCC3-246). Responsible person, Aloysius T. Hepp, organization code 5410, (216) 433-3835.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category 23			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Reaction of metallic indium with benzoyl peroxide in 4-methylpyridine (4-Mepy) at 25°C produces an eight-coordinate mononuclear indium(III) benzoate, $\text{In}(\eta^2\text{-O}_2\text{CC}_6\text{H}_5)_3(4\text{-Mepy})_2 \cdot 4\text{H}_2\text{O}$ (I), in yields of up to 60%. The indium(III) benzoate was fully characterized by elemental analysis, spectroscopy, and X-ray crystallography; (I) exists in the crystalline state as discrete eight-coordinate molecules; the coordination sphere around the central indium atom is best described as pseudo-square pyramidal. Thermogravimetric analysis of (I) and X-ray diffraction powder studies on the resulting pyrolysate demonstrate that this new benzoate is an inorganic precursor to indium oxide. Decomposition of (I) occurs first by loss of 4-methylpyridine ligands (100°-200°C), then loss of benzoates with formation of In_2O_3 at 450°C. We discuss both use of carboxylates as precursors and our approach to their preparation.				
14. SUBJECT TERMS Synthesis; Precursor; Indium oxide; Carboxylate			15. NUMBER OF PAGES 8	
			16. PRICE CODE A02	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	